

Technology

Catalysis

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Surface investigations of tungstophosphoric acid, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, supported on MCM-41 mesoporous silica catalyst

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A Study of Thermal Stability of Tungstophosphoric Acid, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, by XPS, XANES, Hexane Cracking, X-Ray Diffraction and IR Spectroscopy

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Abstract

Tungstophosphoric acid (HPW) is considered as a super acid in a heteropoly acid series that has a Keggin type structure. Heteropoly acids have many industrial applications. It could be used as homogeneous or heterogeneous catalyst. Hence surface characterization is important to understand the reactions that occur on the surface, for example alkylation of aromatics.

Although some studies showed that HPW is a stable molecule up to 600 °C, our work suggests that HPW starts losing stability at temperature as low as 200 °C. High resolution XPS analysis showed a shift of the W 4f peak towards the higher binding energies after heating the acid at 200 °C and 400 °C. In addition, the O 1s peak was shifted towards the lower binding energy that suggests the formation of higher oxidation states of tungsten in the Keggin structure.

Another important feature is that the P 2p peak was not detected at 100 °C but was clearly observed after heating the acid under air at 200°C and 400 °C. This could be explained by the segregation of phosphorous atoms from the center of the HPW molecule to the surface. This means that the structure of the acid molecules on the surface is destroyed, which decreases their chemical stability.

Detailed infrared spectroscopic investigation of the HPW as a function of temperature showed a gradual increase in absorbance of the W-O-W corner shared vibration relative to the absorbance of the other bands. However, the features of the spectra and the absorbance of all the other bands were not changed. This indicates that the symmetry, and hence the stability, of the molecule was decreased upon heating.

Hexane cracking, a surface reaction, was used to investigate the acidity of the surface of the HPW. It was found that the catalyst deactivates completely after 12 minutes at 300 °C. Also no hexane cracking occurred when the acid was heated at 350 °C for 12 hours prior to reaction. This could be explained by the destruction of the surface due to heat and/or chemical reaction.

X-ray absorption near edge structures (XANES) of W N_3 -edge and O K-edge of the HPW were also investigated as a function of temperature. The results will be discussed.

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Surface Investigations of Tungstophosphoric Acid, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, Supported on MCM-41 Mesoporous Silica Catalyst

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A catalyst system of large pore size, such as supported acid on MCM-41, could be more suitable for reactions involving bulk size molecules. The pore size could range from 2.0 to 50 nm. All-silica MCM-41 is not acidic material. However, an acid could be impregnated in MCM-41 to make the surface acidic. Due to its super acidity, tungstophosphoric acid (HPW) was chosen to be impregnated in MCM-41. The surface properties and the stability of the new system are important factors to know for determining what kind of reactions could be used with these systems.

High resolution XPS showed a shift of the W 4f peak towards the higher binding energy after heating the acid under air at 200 °C and 400 °C. This shift was associated with a decrease of the O 1s binding energy. These results suggest the formation of higher oxidation states of the W atom in the Keggin structure of the HPW acid. In addition, the W 4f_{7/2} and W 4f_{5/2} spin-orbit split doublet was not resolved as a result of a drastic broadening of the peaks. This indicates that the impregnation destabilizes the supported acid that may affect its chemical activity.

X-ray absorption near edge structures (XANES) of the W N₃-edge, O K-edge and Si L_{2,3}-edge were also investigated as a function of temperature. The results will be discussed.

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